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The Effect of Superheated Steam on Low Temperature Coking

THE EFFECT OF SUPERHEATED STEAM ON LOW TEMPERATURE COKING

BY

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THESIS

FOR THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

OTTO MEYER HOLZMAN

ENTITLED THE EFFECT OF SUPERHEATED STEAM ON LOW TEMPERATURE COKING.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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INTRODUCTION.

GENERAL: The wide distribution of fuel resources in the United States and the abundant supply of high grade fuels has led to a careless indifference to the efficient utilization of our resources. The unrestricted use of our better grade of fuels and the ruthless waste and neglect of the poorer, but yet valuable fuels, has reached an alarming stage. The present rate with which the supplies of the high grade fuels are being depleted, makes it imperative to conduct scientific research to determine how these resources can best be utilized.

In order to conserve our fuel supply much work is being done on the development of methods to efficiently utilize our poorer grades of fuel. The most important of these are: the utilization of high ash coals; the use of wood refuse and other similar materials; the use of peat and lignites; the use of powdered coal; and the use of producer gas. Quite equal in importance, however, are the investigations conducted to increase the efficiency of our high grade fuels. The most promising results seem to be in the low temperature distillation of coal.

The chief object in modern high temperature coking is to obtain from any given coal the maximum amount of good metallurgical coke at the least consumption of the fixed carbon

of the coal. The first method of coking was by the use of mounds or piles. The coal was placed in large piles with flue spaces that were filled with sufficient wood to ignite the coal. This was covered with sod and allowed to slowly distill for about 5 to 8 days. The yield was very low (50-55%) but due to the high grades of coal then used, the coke was fairly good.

The Beehive oven was an advancement over the mound because it did not require the building and destruction of an oven for each lot of coke. The coal is charged into a heated circular oven shaped like a beehive. The heat required for the distillation of the coal is supplied by burning the liberated volatile products at the top of the oven. This process yields a very hard coke (60-65% yield) in from 48 to 72 hours, depending on the amount of coal charged. It is very wasteful because no attempt is made to recover any of the by-products.

In the by-product ovens a true distillation of coal takes place. Heat is supplied by burning some of the gases of the coal (40-60%) in flues surrounding the oven. The manipulation of the ovens depends, somewhat, on the products desired. Ideal conditions are reached when there is produced a coke, possessing the chemical and physical properties required, together with the maximum yield and quality of by-products. The temperatures used are high (1100°-1300°C.) and the time of coking is from 18-24 hours. The yield is on the average of about 75%.

The coke thus produced is not at all suited for anything but blast furnace work. It is very hard to keep it ignited

unless a forced draft is supplied. This makes it unsuitable for domestic purposes or as a steam coal. The low temperature process, however, produces a cake that is not too hard to be used in place of the less efficient coal. In the burning of coal most of the valuable heat-producing volatile matter goes up the stack unburned and appears in the very disagreeable form of smoke. Thus the removal of the volatile matter at low temperatures would result in the saving of ~~a~~ valuable by-products and the manufacture of a more efficient and smokeless fuel.

The temperatures employed in the low temperature coking process are around 800°C. Below this point many valuable by-products are formed that at higher temperatures will be decomposed into heavy tars. Because of the stability of these compounds at the operating temperatures of this process, much work can be done to control the quantity and quality of some of the desired by-products. The most important among these are the light oils, aromatic compounds and ammonia.

PURPOSE: The purpose of this work was to study the effects of activating atmospheres on the low temperature process of coking that was developed by Prof. S. W. Parr and Dr. T. E. Layng. However, due to difficulties encountered in attempting to carry out this program, it was found advisable to limit the work to the effect of superheated steam only. The interest centered on the nitrogen and sulphur content of the coke.

Present coking practice removes only a very small part of the nitrogen and sulphur originally contained in the coal,

leaving the larger portion in the coke. The nitrogen, while a worthless but not a very harmful element in the coke, would be a valuable product if recovered as ammonia. Most of the nitrogen present in the gas is due to the decomposition of ammonia. If this decomposition could be prevented, it would reduce the nitrogen (an inert element) content of the gas, and increase the ammonia yield. Due to the fact that coking removes only a small part of the sulphur from the coal, the supply of coking coals is limited. Sulphur is a very undesirable element in most operations where coke is used.

It was hoped that the use of low pressure steam superheated to 600°C. would reduce the nitrogen and sulphur content of the coke without greatly effecting the quality and the yield. It was desired to remove the nitrogen as ammonia and the sulphur as hydrogen sulphide.

HISTORY: The work on the low temperature coking of coal was started at the University of Illinois under the direction of Prof. S. W. Parr, who is still conducting this investigation. The original purpose of the work was to develop a more efficient and smokeless fuel from Illinois coals. C. K. Francis worked at this phase of the problem.during 1907-8.

H. L. Olin continued this work on a small scale but turned his efforts "to discover some fundamental facts pertaining to the properties and characteristice of bituminous coals". He suceeded in developing several facts concerning the principles

involved in the formation of coke. Later he worked on a larger scale to enable him to conduct a detailed study of the yield and value of the by-products on a commercial basis. By mixing Illinois coals with the breeze obtained from former coking experiments he was able to get a sound coke at a temperature of 500°C.

Dr. T. E. Layng conducted his experiments at higher temperatures (750°C.) and found a method which enabled him to coke all grades of Illinois coals. Briefly the process as discovered and developed by Prof. S. W. Parr and himself consisted of, first preheating the coal in a ratating container to a temperature of about 250°C. and then placing this coal into a retort previously heated up to 800°C.

The preheating removes all the moisture while the coal is heated to a temperature that is below the point of decomposition. On being placed into the retort the heat from the sides is conducted through the coal at a rate that keeps the temperature of the entire mass almost the same throughout. An exothermic reaction takes place that quickly raises the temperature of the entire charge to a state where the coal begins to soften (the first stage of coking) without the formation of an outer shell of coke. The volatile products can escape through all parts of the mass. In the high temperature process the coking starts at the walls and travels slowly towards the center. The outer shell of coke offers less resistance to the gases than the pasty mass next to it so that they pass through the highly heated zone against the direction in which

the heat is applied.

The temperature of 750°C. was chosen as an upper limit of heating because several reactions take place or are completed at this point. Below 750°C. all the heavy hydrocarbons are expelled, giving a gas high in illuminants and a large yield of low boiling condensible oils. This temperature is also low enough so that practically no secondary decomposition takes place. Above 750°C. a lean gas consisting mainly of hydrogen and methane is given off and the volatile products are subject to decomposition, forming heavy tars. Higher temperatures also cause the decomposition of ammonia with the result that the gases contain much nitrogen.

Due to the recent development of the low temperature coking process, very little work on the use of activating atmospheres has been done. C. A. King in the laboratory of the Farnley Iron Works carried out a very complete set of experiments working on a very small scale. He heated coke in a silica tube to 800°C. and passed different gases over it. He found that mixtures of carbon monoxide, carbon dioxide and nitrogen had little or no effect on the nitrogen of the coke when passed through the tube. Dry hydrogen liberated only about 10% of the nitrogen as ammonia. Hydrogen gas saturated with water at 85°C. greatly increased the ammonia yield and used up only from 2-5% of the coke. It was found that a coke such as is made in the Beehive ovens gives up only a very small percent of its nitrogen as ammonia. Efforts to reproduce these results on a commercial scale have been unsuccessful.

THEORETICAL: At present only a very small part of the nitrogen of coal is recovered as ammonia. In average practice about 18-20 lbs. of ammonium sulphate (10-15% of the total nitrogen) are obtained per ton of coal coked. The major portion 60-70% remains in the coke in a very complex condition, seeming to merely be a surface compound, that is the nitrogen is just attached to the carbon of the coke but forms no definite chemical compound. A small percent of the nitrogen stays in the tar and 10-15% appears in the gases as nitrogen. If the decomposition of the ammonia due to the contact of the gases with the hot sides of the retort could be reduced, the nitrogen content of the gas would be decreased and the ammonia yield increased. This, however, is a very small quantity compared with the nitrogen that is left in the coke.

In some of the gasing processes the decomposition of the ammonia is prevented by the rapid removal of the gases from the heated zones, or by the use of such catalytic agents as calcium oxide or ferric oxide. In the manufacture of producer gass by the Mond process, a conversion of about 70% of the nitrogen of the coal into ammonia is obtained. The producer is operated with an excess of steam (2.5 lbs. steam to 3 lbs. of air preheated to 250°C.) two-thirds of which remains undecomposed. The temperature is, therefore, kept low, about 600°C., sacrificing the quality of the gas. It seems that as the coke is destroyed the nitrogen combines with the hydrogen, liberated from the decomposition of the water, forming synthetic ammonia.

Since the temperature is low very little of the ammonia is decomposed (ammonia is not stable above 800°C.). The main loss of ammonia is by oxidation, but the presence of the excess steam keeps this loss down to a minimum. In the manufacture of water gas there is a similar synthetic formation of ammonia, but the high temperatures (1300-1500°C.) result in its decomposition.

By steaming near the end of the low temperature coking run it was expected to produce results similar to those obtained in the Mond process. Condition, however, are somewhat different in the two cases. In producer gas manufacture it is desirable to convert all the coke into gas. Thus the removal of the carbon leaves the nitrogen (if it exists as a surface compound) free to form synthetic ammonia with the hydrogen. In the coking process it is desired to obtain as large a yield of coke as possible, so that the nitrogen must be removed with as little harm to the coke as possible. In the latter case it was attempted to replace the nitrogen by some other gas, presumably hydrogen.

The sulphur of coal occurs in three important forms; the organically combined sulphur of the humus materials; the organically combined sulphur of the resinic bodies; and the pyritic sulphur. The first two forms are only a small part of the totals. During coking, part of the humus and resinic sulphur volatilizes and about half of the pyritic sulphur is removed. The sulphur remaining in the coke exists in an entirely new form. The pyritic sulphur does not, as is generally believed, remain as ferrous sulphide but exists as a surface compound similar to the condition of the nitrogen. This compound is extremely stable even

at high temperatures, resisting the action of strong acids and oxidizing agents. If it is a true surface compound an active gas such as hydrogen (formed by the decomposition of the water by the coke) should remove the sulphur as hydrogen sulphide.

EXPERIMENTAL.

APPARATUS: The apparatus used in this work was designed and erected by Dr. T. E. Layng. Fig.I shows the retort and washing train. A is the retort, cylindrical in shape, capable of holding from 30 to 40 lbs. of coal at a charge; the internal diameter is 7 3/4 ins. and the height about 40 ins. The heat is applied by means of an electric current sent through five coils so that the maximum temperature obtainable with the empty retort is 800°C. By means of external resistance the temperature and rate of heating can be very closely regulated. The retort is set in a 22 inch square frame work and packed with sil-o-cel. The coal is charged in through the cap, A^1. The bottom is dropped down by removing several bolts. A^2 shows the thermocouple pockets, that extend about 18 ins. up into the furnace; one is on the outside, and the other in the center of the retort. A^3 is an opening through which the steam is admitted.

The gases pass off through the air-cooled take off pipe as shown in the illustration, and deposit most of their tar in B, a two-liter glass flask. D is a water-cooled condenser that cools the gases, removing some of the tar and water that collect in the separating funnel C. D^1 is a small chamber filled with pebbles, which act as baffles, so that the gases should lose most of their entrained moisture. If valves 1 and 2 are open and valve 3 closed, the gases pass through E, F, and G. E is a chamber filled with scrap iron, where all the remaining entrained

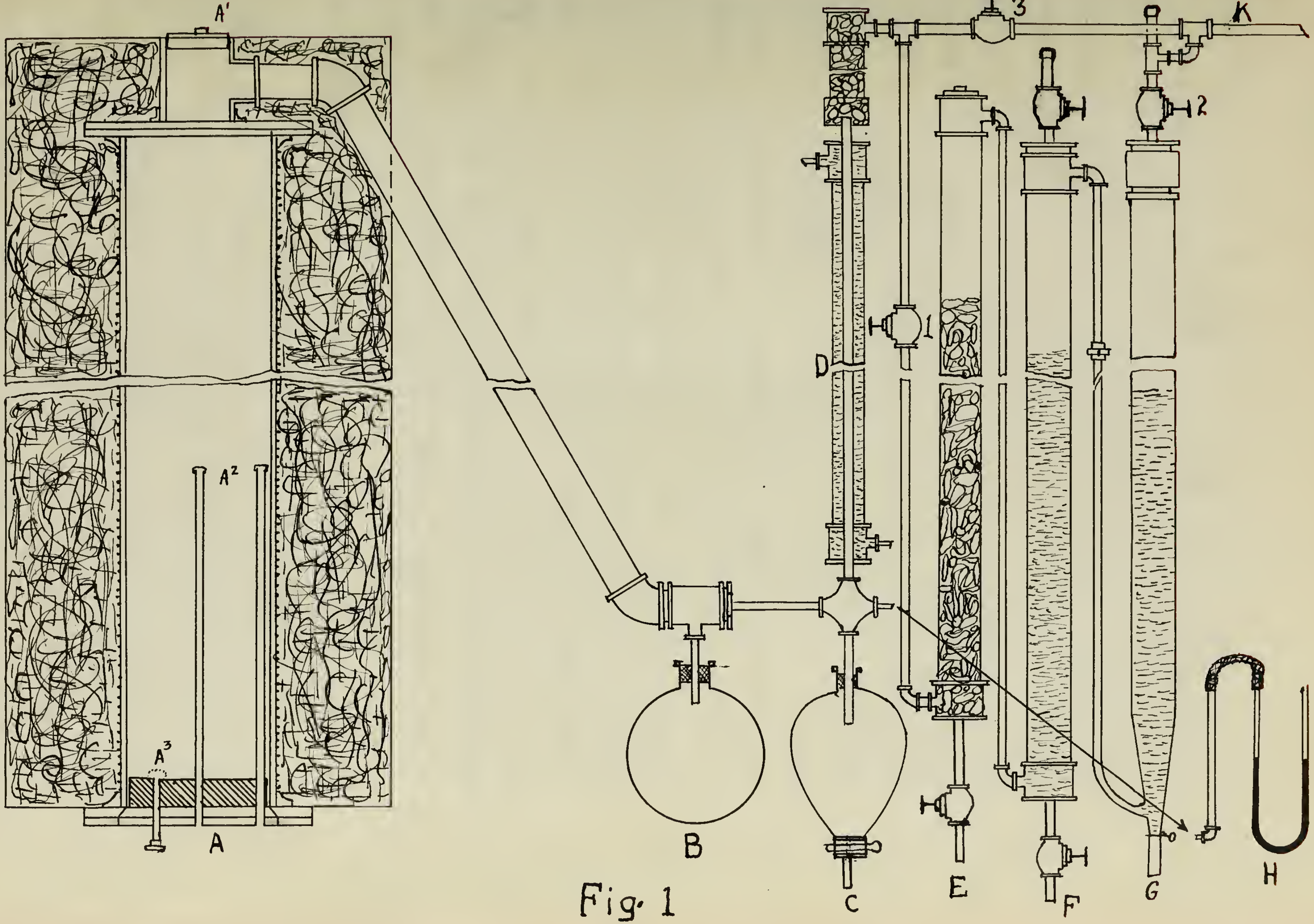

Fig. 1

moisture and tar is removed. The next chamber F, is filled with a wash oil to take out all the condensable hydrocarbons. G is a lead pipe filled with dilute sulphuric acid to take out the ammonia. H is an open-end mercury manometer placed on the take-off pipe so that the pressure conditions in the retort can be controlled. K is the pipe leading to the exhauster. By opening valve 3, and closing valves 1 and 2, the gases are "by-passed" directly through the exhauster without entering the washing train.

Fig. II shows the exhauster and gas-collecting tanks. There are three tanks each having a capacity of 27.5 cu.ft., being 3 ft. in diameter and 48 ins. high. They are sealed by water and balanced with counter weights. The gases, as they leave the washing train through K, enter the exhauster M. The valve L, is a by-pass so that by regulating it any desired pressure in the retort can be obtained. The gases enter the tank by opening the valve N or N^1 and pass through P or P^1 through the bottom of the tank and are discharged by a pipe that extends to the top of the interior of the tanks. By means of the valve O and O^1 one tank may be emptied, while the other is being filled. The piping system makes each tank independent of the others.

The superheater, which was connected to A^3, was made from a 40 in. length of 2 in. piping. One end was plugged and the other had a thermocouple pocket reaching in about 15 ins. The steam passed from the high pressure main through a separator and was discharged into the retort through A^3. The heating was accomplished by means of an electric current sent through nichrome wire. A temperature of about 650°C. was maintained,

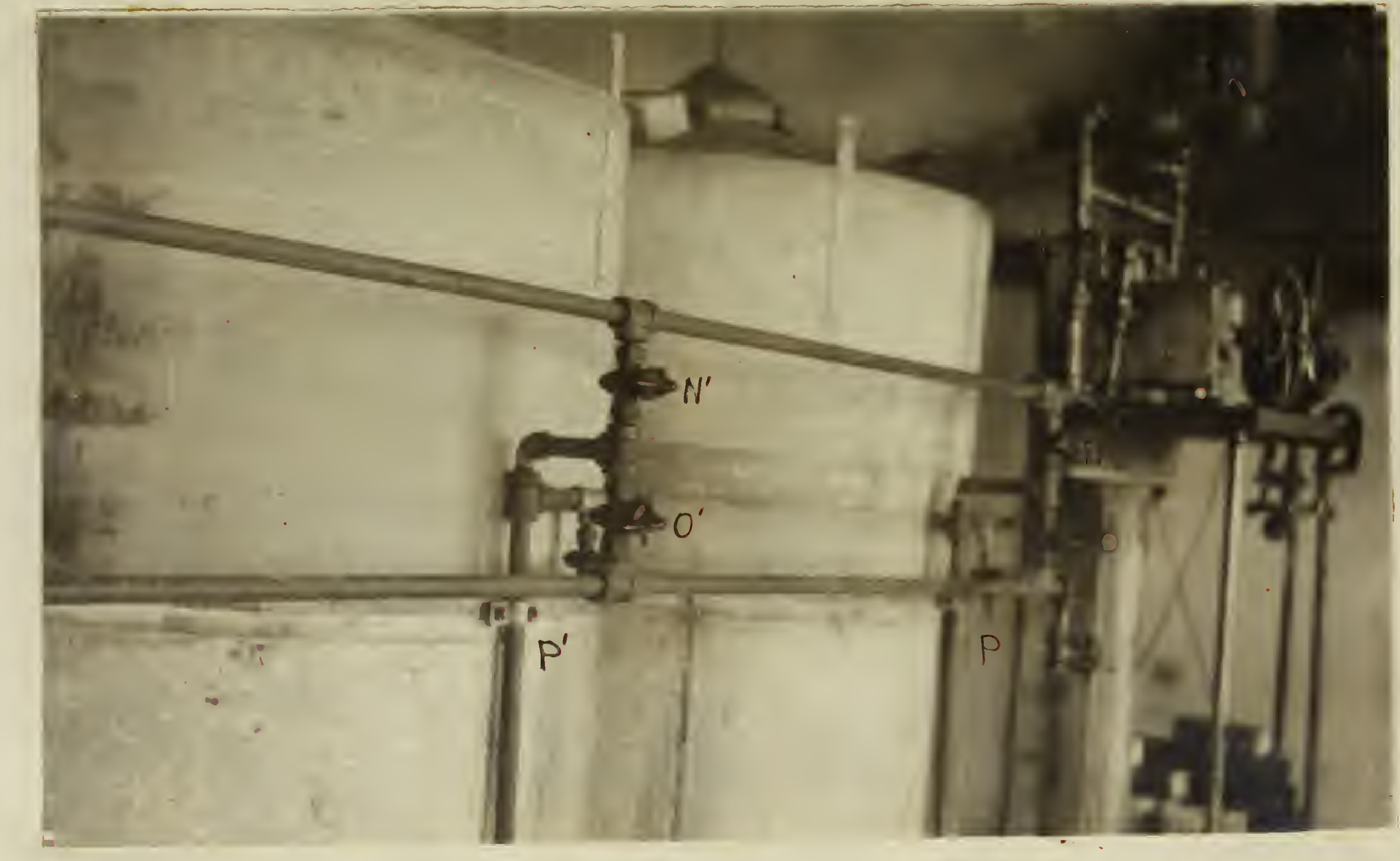

Fig. II

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when slow stream of dry steam was flowing through. The heat insulation consisted of a packing of sil-o-cel in a 14 in. cylindrical frame.

The preheater was an 18 in. cylindrical sheet iron container about 30 ins. long and tapering to a 2 in. opening at one end. It was heated by being rotated over a gas flame for about 15 minutes. By means of a block and tackle the preheater was raised to the top of the retort to discharge its contents.

Three thermocouples were made to be used in this work. Since the highest temperature was to be 800°C., iron and container were chosen for elements. Equal lengths of iron and constantan wire were cut. One end of each couple was twisted together and welded. A. Hoskins millivoltmeter was used to record the temperatures but it was found that the voltage was too high for the meter. To remedy this a small spool of copper wire was attached to the top of the couple which supplied enough resistance to make the readings correspond very closely to the actual temperature. These couples were then wired up and calibrated against a standard platinum platinum-iridium couple. By means of a switch all three couples were read from the same millovoltmeter. Later in the year these couples were re-calibrated and found to be off only 10°C.

OPERATION: The retort was constructed so that it would heat up very slowly. It was, therefore, necessary to turn on the current some 12 hrs. before the run was started. A charge of 33 1/3 lbs. of coal, ground to buckwheat size, was used. This was placed

into the preheater and slowly revolved over a gas burner until a temperature of approximately 250°C. was reached. The time required was about 15 min. The charge, by the aid of a block and tackle, was then quickly transferred into the heated retort, where the coking was allowed to proceed. By the use of the exhauster a pressure of about 1/8 in. mercury was maintained throughout the run. This was kept so in order to prevent the leakage of air into the retort or any other part of the system.

Temperature readings of the steam admitted, and the temperature of the center and the outside of the charge were recorded every 15 min. A run was considered complete when the temperature of the center of the mass was equal to that of the outer edge. After the power was turned off the retort was allowed to stand about 36 hrs. to cool. By removing the bottom plate the charge would fall out. If it hung,an iron rod was used to poke it down.

The time that the steam was admitted was changed in each run in order to find at what stage it was most beneficial. The temperature of the steam was also varied. Temperatures of 500°C. and 600°C. were used. A run without the use of steam was later made so that the results could be compared.

Some experiments were carried out in order to find a means of measuring the amount of steam that was being added to the retort. Due to the low pressures used it was impossible to use a calibrated orifice. A by-pass was tried intending to condense and measure a definite portion of the steam used. This

was found unsatisfactory because of the pressure variations in the retort. It required, in order to give satisfactory results, that a pressure exactly equal to the atmosphere should be maintained throughout the entire run. It was not found possible to do this. An approximate determination of the steam added could be obtained by measuring the total condensed water,after a run,and subtracting from this the water of decomposition. This would not, however, give any means of determining the amount of water that was decomposed.

METHODS OF ANALYSIS: The nitrogen was determined by the standard Kjeldahl-gunning method. Sulphur in the coal, coke, and tar was determined by a peroxide bomb fusion, and precipitated as barium sulphate. Sulphur in gas was determined by burning a measured portion and washing the resulting gases in a 5% sodium carbonate solution, to which a few drops of bromine water had been added (Drehschmidt process). It was first attempted to determine the sulphur in gas by the absorption of the sulphur-dioxide(formed by the burning of the sulphur compound in the gas) with moist ammonium carbonate; but due to the difficulty of thoroughly leaching out the ammonium sulphite formed, this method was abandoned. The gas was analyzed in a modified Orsat apparatus. The carbon dioxide was removed by potassium hydroxide; the oxygen,by sodium pyrogallate; the ethylene, by bromine water or concentrated sulphuric acid; the benzene, by fuming sulphuric acid; the hydrogen and carbon monoxide, by passing them over copper oxide heated to 300°C., absorbing the

carbon monoxide in potassium hydroxide as carbon dioxide, and recording the contraction as hydrogen; the methane and ethane, by combustion and oxygen. The nitrogen is determined by difference from 100%.

COAL USED: The allotted supply of coal was not sufficient to complete this work, so a new supply was obtained. This, however, was not the same kind of coal as that used in the first experiments. The first was a fresh good grade of Illinois coal. The second was a lot of badly weathered Illinois coal from Vermilion County. The results obtained with the second coal will be used since numerous errors were introduced in the first experiment that were later eliminated. Analysis of this coal is given in Table A.

Table A. Analysis of Coal.

Proximate Analysis. (Air-dry sample)

Ash	Moisture	Volatile	Fixed Carbon
13.40%	2.80%	36.10%	47.70%

Air-drying losses 3.54%.

Ultimate Analysis. (Ash and Water Free.)

Hydrogen	Carbon	Nitrogen	Oxygen	Sulphur
5.40%	79.00%	1.55%	10.75%	3.30%

DISCUSSION AND PRESENTATION OF DATA.

CONDITIONS OF COKING: As shown in Table I, steaming prolonged the time of coking in all cases. This was due to the endothermic reaction between the steam and the coke. The time required for test runs 6, 7, and 8 was the same even though the temperature of the steam and the time that it was used were different. This indicated that the reaction of the steam and the coke started at some point below 500°C. It brought out the fact that it is useless to admit steam into the retort, when the temperature of the coke is below 500°C.

Test run No. 9 was shorter in duration than the other runs where steam had been added, because the time that the endothermic reaction could proceed was shorter. The results obtained, however, were about the same as in the other runs. Results of test runs No. 9 and No. 10 will be used to study the effects of steaming on the by-products.

The coke obtained from runs No.4-6 inclusive, in which steam was used, was just as sound as that obtained from run No.3 where no steam was used. Test runs No.7-10 inclusive were made with weathered coal. The product here obtained did not form a coherent coke even when no steam was admitted. In both cases steam had no effect on the physical condition of the coke.

Table I. Temperatures and Conditions of Test Runs.

	Temp. of retort at start of run °C.	Temp. of Preheating	Temp. of Retort when Steam was Admitted °C.	Average Steam Tempe °C.	Time of Coking hrs.	Time Steam was used hrs.	Final Temp. °C.
Test Run No. 3	620	250	No Steam	---	6	---	795
Test Run No. 10	625	270	No Steam	---	6½	---	760
Test Run No. 6	600	200	At Start	500	8½	8½	730
Test Run No. 7	640	220	At Start	625	8	8	725
Test Run No. 8	600	250	475	500	8½	4	695
Test Run No. 9	610	200	600	625	7	2½	720

YIELD AND QUALITY OF PRODUCTS: A small percent (3.4%) of the coke (Table II) was destroyed by the steam. This loss was part of the volatile matter (Table III) and some of the fixed carbon of the coke. The removal of the volatile matter was doubtless due to the reduced vapor pressure in the retort caused by the steam.

Table II. Yield of Products.

	% Yield of Coke	% Yield of Tar	Yield of Gas per ton Coal	Ammonium Sulphate lbs. per ton
Test Run No. 9	64.8	4.85	8,860 cu.ft.	25.80
Test Run No.10	68.2	4.45	6,225 cu.ft.	18.05

Table III. Proximate Analysis of Dry Coke.

	Volatile %	Fixed Carbon %	Ash %
Test Run No. 9	3.18	74.52	22.30
Test Run No.10	5.14	73.76	21.10

No accurate tests of the quality of the tar were made. On distillation of tar No. 9, however, a solid hydrocarbon was obtained, while at the same point tar No. 10 gave a liquid product. The steam, by reducing the vapor pressure, aided in the distillation of some of the heavier tars; thus increasing the tar yield.

The gas obtained from test run No. 9 had a lower heat value than that obtained from run No.10 (Table IV). This is due to the large amounts of CO_2 and H_2 that were formed, because of the low temperature at which the steam was decomposed. The difference in nitrogen content may be due to an error since it was determined by difference.

Table IV. Gas Analysis.

	Test Run No. 9 (% by vol.)	Test Run No. 10.
CO_2	13.1	7.8
O_2	.8	.8
C_2H_4	.8	1.1
C_6H_6	.9	1.4
CO	8.6	5.9
H_2	55.0	48.8
CH_4	15.3	26.4
C_2H_6	3.5	4.1
N_2	2.0	3.7
B. T. U. (Calc.)	470	588

A 43% increase in the yield of ammonia was obtained by the use of steam. This was doubtless due to the synthetic formation of ammonia by the combination of the hydrogen with the nitrogen of the coke. While some of the coke was destroyed during this action, the formation of ammonia did not depend upon that reaction. The destruction of the coke was only necessary to furnish the hydrogen. The reaction seemed to be just a replacement, where the hydrogen replaced the nitrogen, favoring the reaction between the two gases to form ammonia. The increase of the total quantity of nitrogen recovered was very small. However, by varying the conditions somewhat a point may be reached where the conversion into ammonia will be much larger.

EFFECT ON THE SULPHUR: As shown in Table V, steam has some effect on the sulphur of the coke. The reaction seems to be similar to the replacement of nitrogen with hydrogen, only in this case the sulphur is replaced by hydrogen, and is removed as hydrogen sulphide. The fact that a little (4.5%) sulphur was removed

SUMMARY.

I. Steaming prolongs the time of coking.

II. Steam does not affect coking until after the coke structure is formed. This is above 500°C.

III. Steaming does not affect the physical condition of the coke.

IV. Steaming slightly decreases the coke yield, due to the decomposition of the steam. The ammonia yield is increased, due to the synthetic formation of ammonia. The gas yield is increased, but the B. T. U. value is decreased because of the large amounts of CO_2 and H_2 formed. A slight increase in the yield of tar is obtained.

V. Steaming will remove some of the nitrogen and sulphur from the coke, but the conditions that give the best results have not been found.

indicates that there is a possibility of improving the conditions so that an appreciable quantity may be removed.

Table V. Distribution of Sulphur.

	Test Run No. 9.		Test Run No. 10.	
	% Sulphur	% of total Sulphur	% Sulphur	% of total Sulphur
Coal	2.77	100.0	2.77	100.0
Coke	2.20	49.7	2.20	54.2
Tar	1.57	2.6	1.53	2.4
Gas (by diff.)		47.7		43.4

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